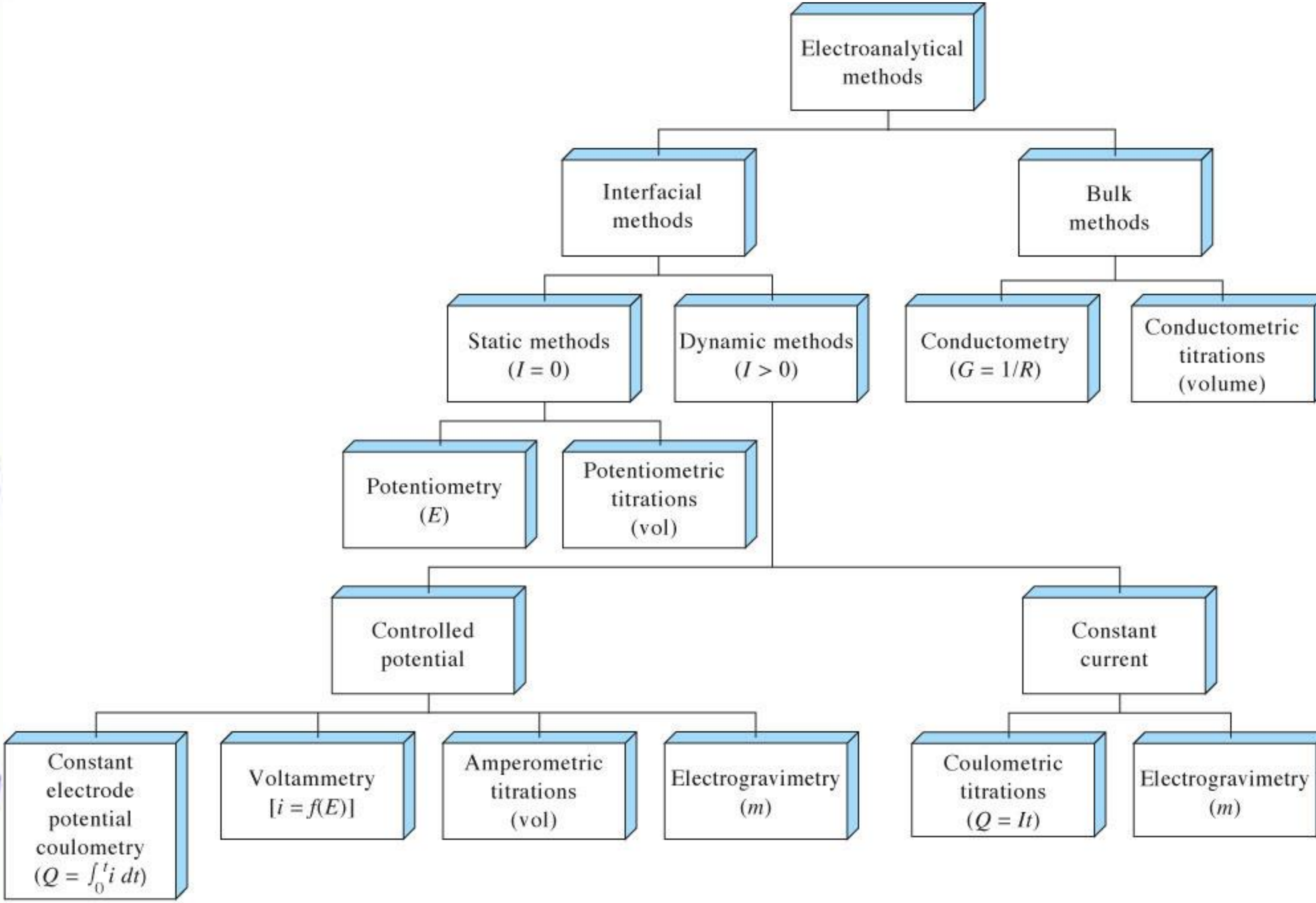
Chemistry 4631

Instrumental Analysis

Lab Lecture 3

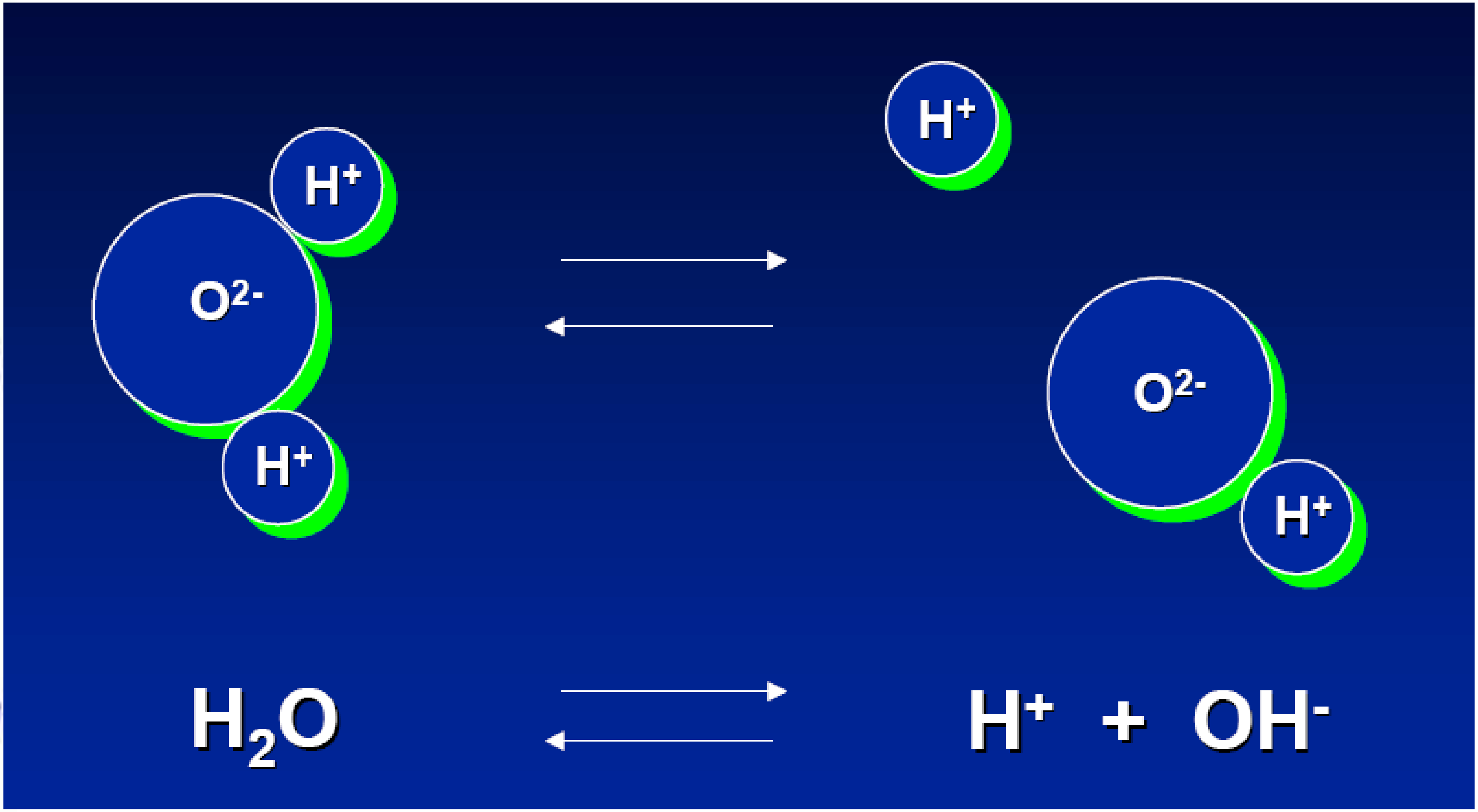
Conductivity


Electroanalytical methods
Interfacial methods
Bulk methods
Static methods ($I = 0$)
Dynamic methods ($I > 0$)
Conductometry ($G = 1/R$)
Conductometric titrations (volume)
Potentiometry (E)
Potentiometric titrations (vol)
Controlled potential
Constant current
Constant electrode potential coulometry ($Q = \int_0^t i\,dt$)
Voltammetry [$i = f(E)$]
Amperometric titrations (vol)
Electrogravimetry (m)
Coulometric titrations ($Q = It$)
Electrogravimetry (m)

Conductivity

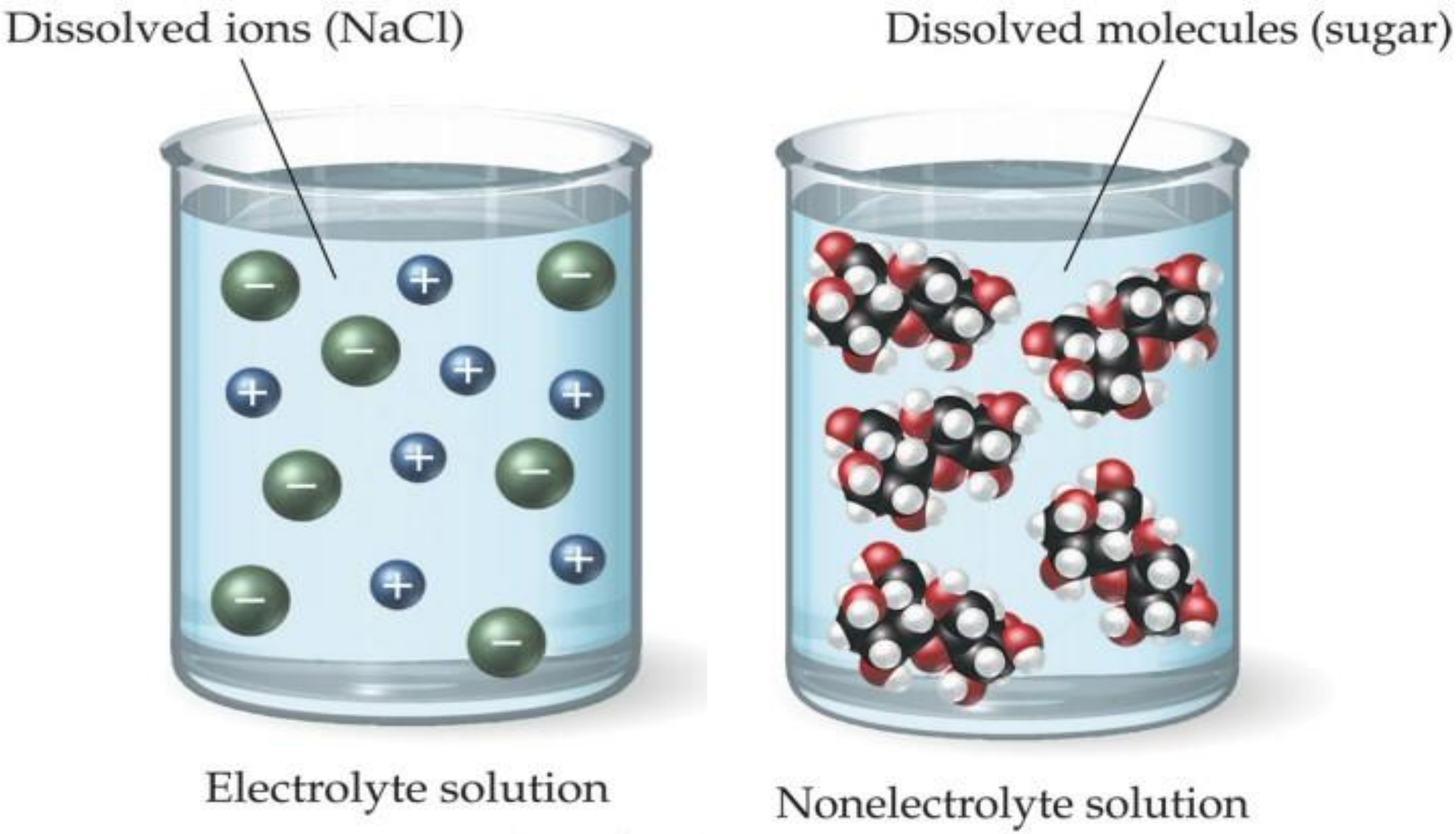
A measure of how well a solution conducts electricity

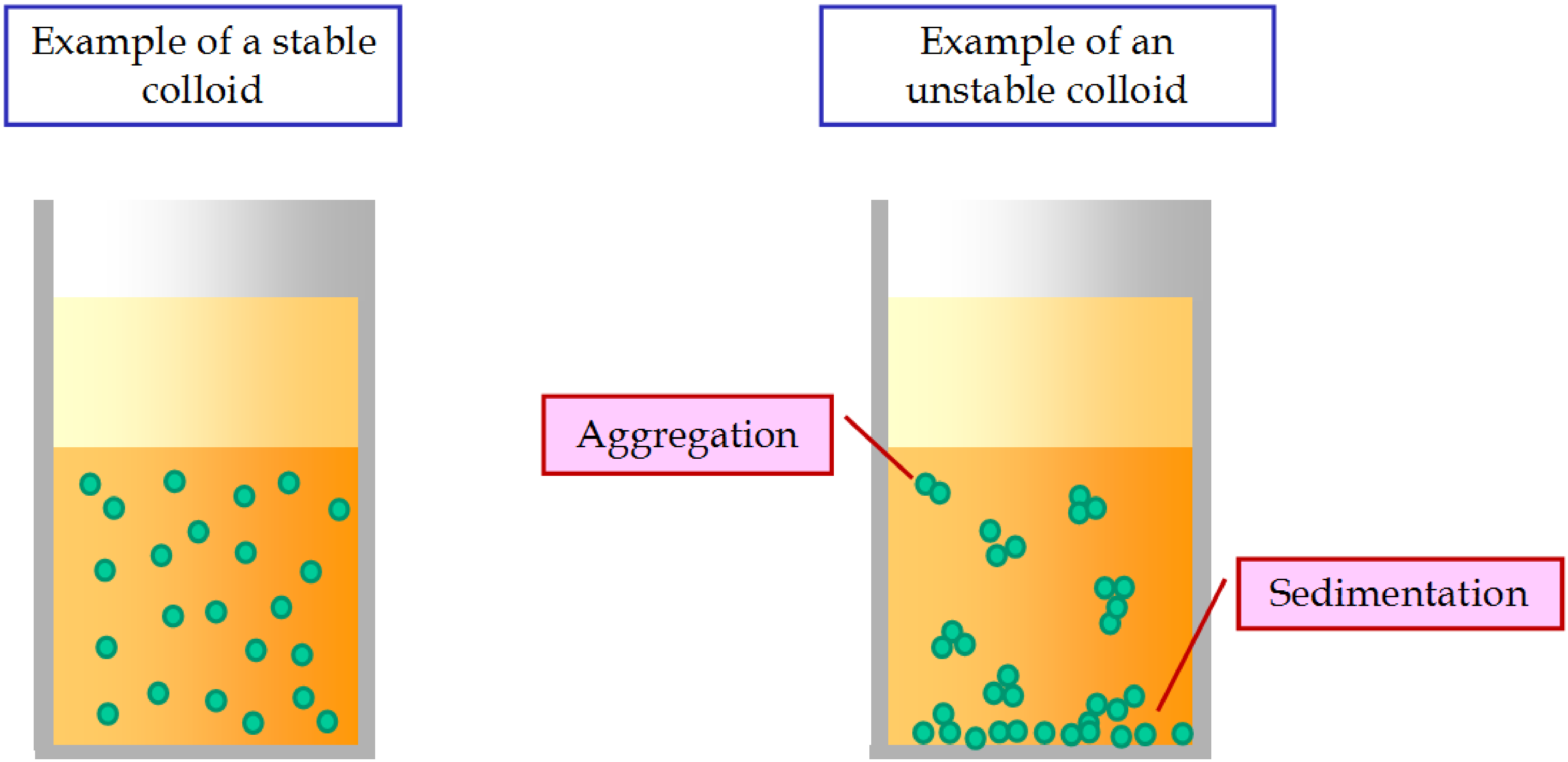
- Water with absolutely no impurities (does not exist)
    - Conducts electricity very poorly
- Impurities in water increase conductivity
    - When measure conductivity of water can estimate the degree of impurities

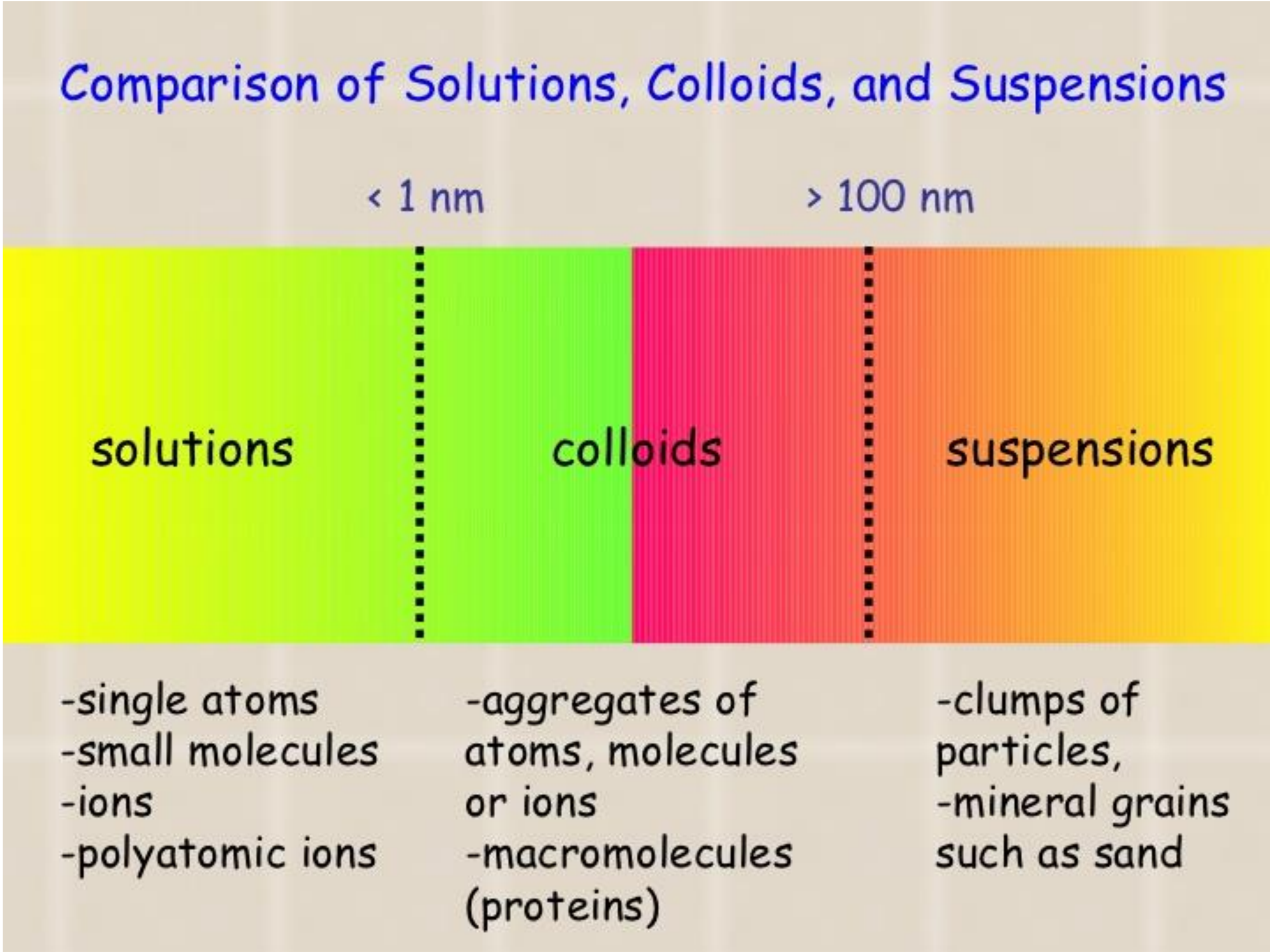

H^+
O^{2-}
H^+
H^+
O^{2-}
H^+
$H_2O \rightleftharpoons H^+ + OH^-$

Conductivity

- **Electrolytes**
  - Substances whose aqueous solution is a conductor of electricity.
- **Strong electrolytes**
  - All the electrolyte molecules are dissociated into ions.
- **Weak electrolytes**
  - A small percentage of the molecules are dissociated into ions.
- **Nonelectrolytes**
  - None of the molecules are dissociated into ions.


Dissolved ions (NaCl)
Dissolved molecules (sugar)
Electrolyte solution
Nonelectrolyte solution


Example of a stable colloid
Example of an unstable colloid
Aggregation
Sedimentation


Comparison of Solutions, Colloids, and Suspensions
< 1 nm
> 100 nm
solutions
colloids
suspensions
-single atoms
-small molecules
-ions
-polyatomic ions
-aggregates of
atoms, molecules
or ions
-macromolecules
(proteins)
-clumps of
particles,
-mineral grains
such as sand

Conductivity

The current is carried by dissolved ions.

The ability of an ion to carry current is a function of:

- Ion charge (more charge, more current)
- Ion mass or size (larger ions, conduct less)
- Concentration of ions
- Temperature of solution

Conductivity

- Conductivity (G), the inverse of resistivity (R) is determined from the voltage and current values according to Ohm's law

$$\mathbf{G = 1/R = I\ (amps) / E\ (volts)}$$

Conductivity

- **Conductance *G* in S**

$$G = \frac{1}{R} \qquad\qquad G = \kappa \frac{A_s}{l}$$

- κ in equation is **conductivity**. In S m^{-1}.

- **Molar conductivity** (in S m^2 mol^{-1})

$$\Lambda_m = \kappa / c$$

Conductivity

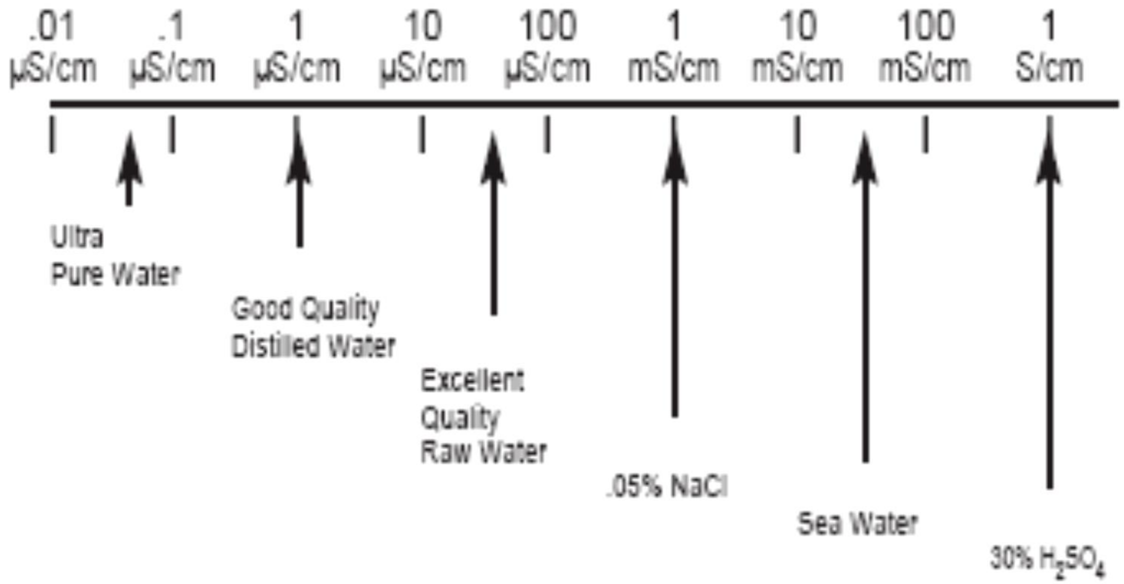
- **Basic unit of conductivity**
  - Siemens (S), formerly called the mho
  - Cell geometry affects conductivity values
  - Standardized measurements are expressed in specific conductivity units (S/cm) to compensate for variations in electrode dimensions
  - Specific conductivity (κ) is the product of measured conductivity (G) and the electrode cell constant (L/A)
    - L: length of the column of liquid between the electrode
    - A: area of the electrodes

$$\kappa = G \times (L/A)$$

Conductivity

- **Solution**
  - Absolute pure water
  - Power plant boiler water
  - Good city water
  - Ocean water
  - 31% HNO_3

- **Conductivity**
  - 0.055 µS/cm
  - 1.0 µS/cm
  - 50 µS/cm
  - 53 mS/cm
  - 865 mS/cm



Conductivity

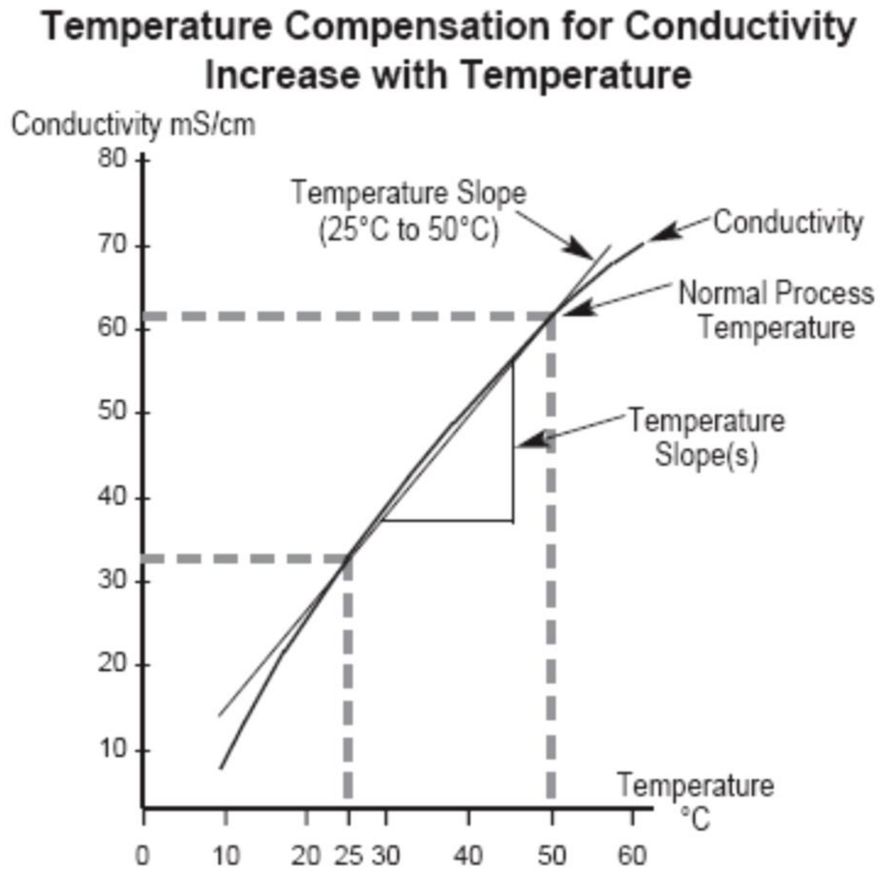
- Conductivity measurements are temperature dependent
  - The degree to which temperature affects conductivity varies from solution to solution
  - Calculated using the following formula:
  - $\mathbf{Gt = Gt_{cal} \{1 + \alpha(T - T_{cal})\}}$
    - **Gt = conductivity at any temp T in °C**
    - **Gt_{cal} = conductivity at calibration temp T_{cal} in °C**
    - **α = temperature coefficient of solution at T_{cal} in °C**

Conductivity

- Common alphas (**α**) are listed in tables
- To determine α of other solutions
  - Measure conductivity at a range of temperatures
  - Graph the change in conductivity versus the change in temperature
  - Divide the slope of the graph by Gt_{cal} to get α

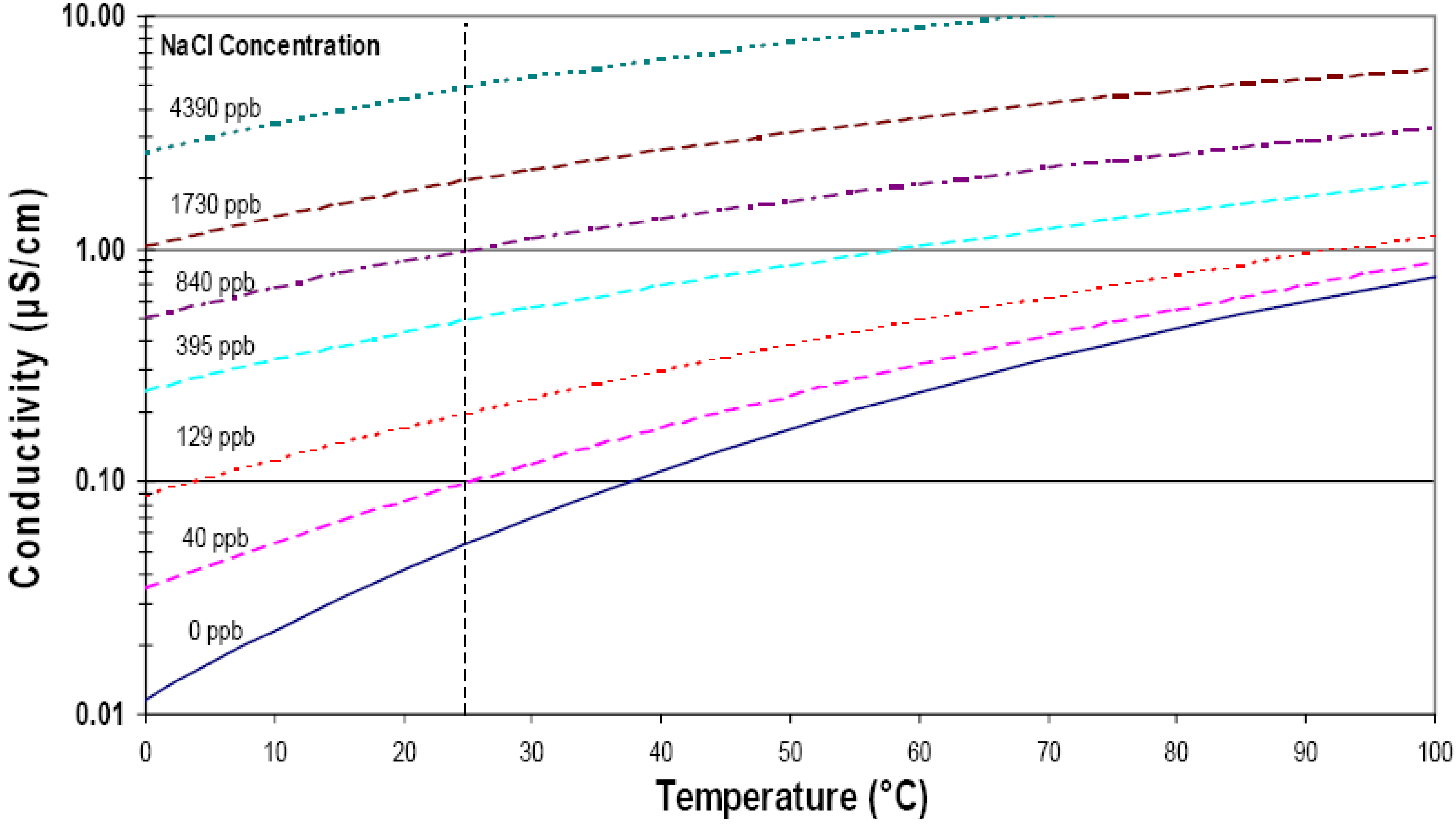
Conductivity

Conductivity of a solution typically increases with temperature.



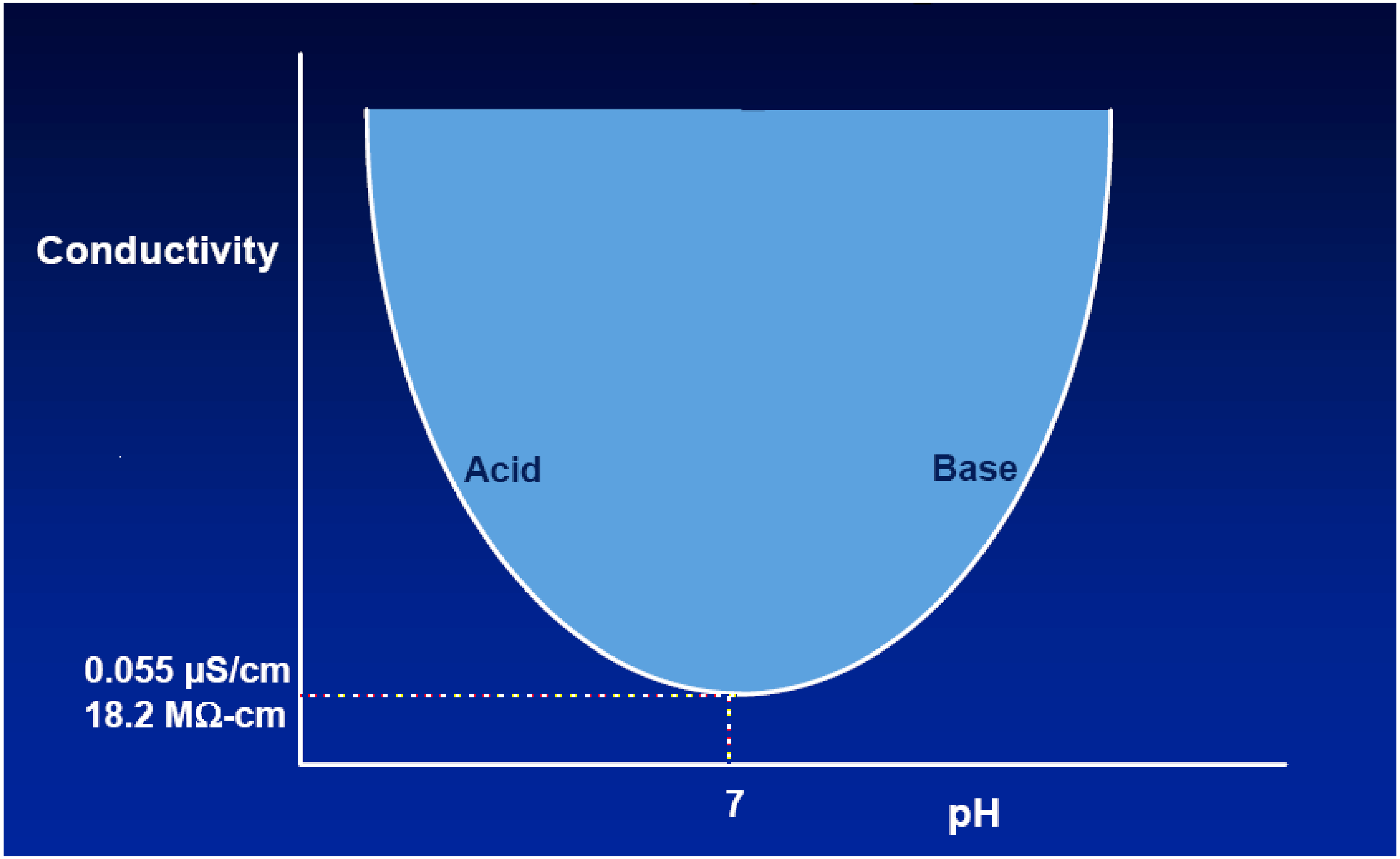
Conductivity

Conductivity and Temperature



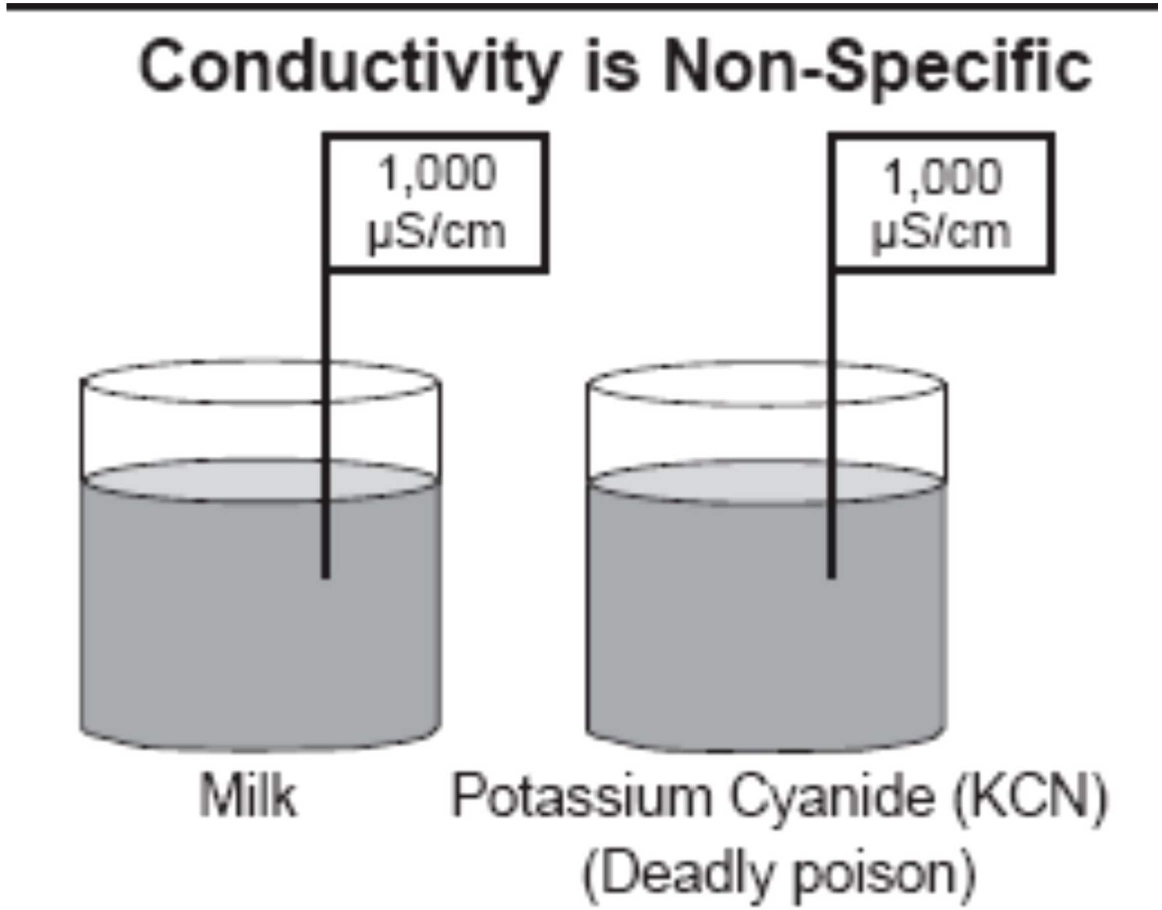
Conductivity

Conductivity vs. pH



Conductivity

Conductivity is Non-Specific



Conductivity

Instrument consist of

Electrode

Meter

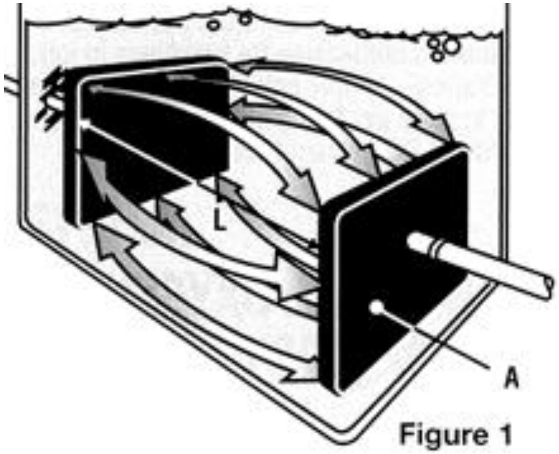


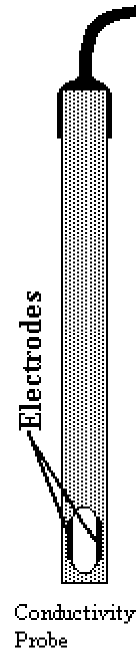
Figure 1

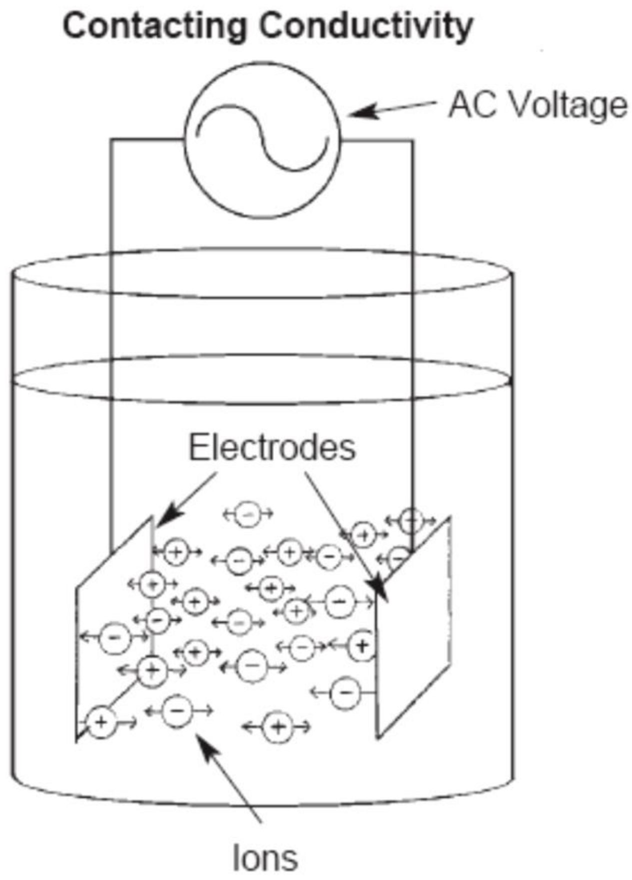
- Conductivity is measured by
  - Two plates placed in the sample
  - Potential is applied across the plates and current is measured

Conductivity

Conductivity Electrode

- 2 metals in contact with electrolyte solution
- Voltage is applied to electrodes and resulting current that flows btw electrodes is used to determine conductance
- Amount of current flowing depends on:
  - Solution conductivity
  - Length, surface area, geometry of electrodes





Conductivity

Conductivity Measurement

- Specific conductivity (κ) is the product of measured conductivity (G) and the electrode cell constant (L/A)
    - L: length of the column of liquid between the electrode
    - A: area of the electrodes

$$\boldsymbol{\kappa = G \times (L/A)}$$

where L/A is called the cell constant Kc

Conductivity

Cell constant depends on:

– area of plates

– distance between plates

Conductivity

Conductivity Measurement

- Apply an AC Voltage to Two Electrodes of Exact Dimensions
- Acids, Bases and Salts (NaCl) Dissolve in Solution and Act as Current Carriers
- Current Flow is Directly Proportional to the Total Dissolved Solids in Solution
- Physical Dimensions of a Conductivity Electrode are Referred to as the Cell Constant
- Cell Constant is Length/Area Relationship
  - Distance Between Plates = 1.0 cm
  - Area of Each Plate = 1.0 cm x 1.0 cm
  - Cell Constant = 1.0 cm^{-1}

Conductivity

Sample Measurements

- Rinse the conductivity cell sensing element with DI water between sample
- Dip cell up and down in sample 2-3 times to completely wet surface
- Allow air bubbles to escape from conductivity cell side holes by tilting cell slightly
- It is important to control sample temp
  - Since reading will continue to drift until the temp has stabilized

Conductivity

Storage

- 1. Best to store conductivity probe so that electrodes are immersed in DI water
- 2. Can also store dry
  - Before use:
  - Probe should be soaked in DI water for 5-10 minutes
  - To assure complete wetting of the electrodes

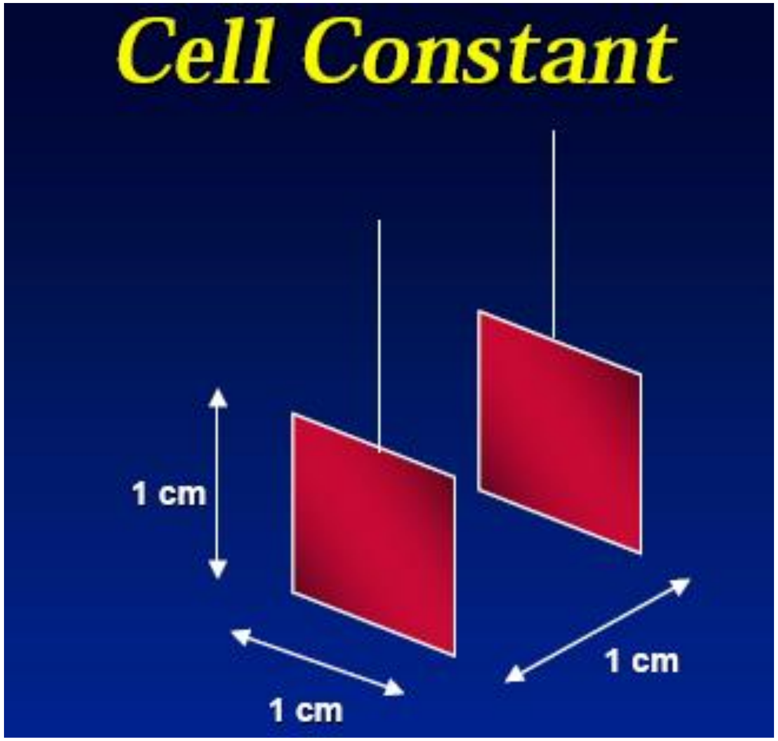
Conductivity

Cleaning

- 1. For most applications, a hot solution of water with mild lab detergent can be used for cleaning
- 2. Dilute 1% nitric acid may be used followed by DI water rinsing

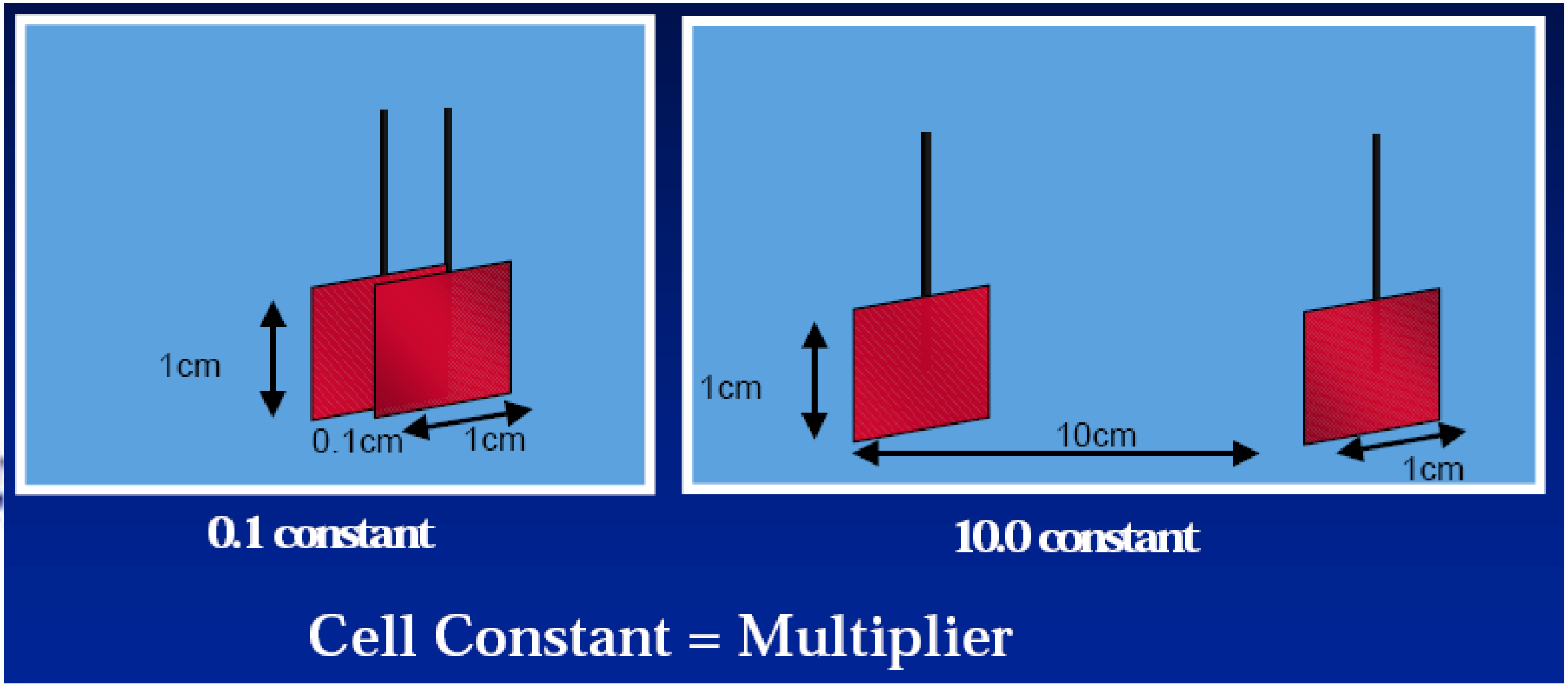
Conductivity

- Cell constant:
  – Measure of current response of a sensor conductive solution
  – Due to sensor's dimensions and geometry
  – Units: cm^{-1} (length divided by area)



$$\text{Conductivity Cell Constant} = \frac{\text{Length}}{\text{Area}} = \frac{1\ \text{cm}}{1\ \text{cm}^2} = 1\ \text{cm}^{-1}$$

Conductivity

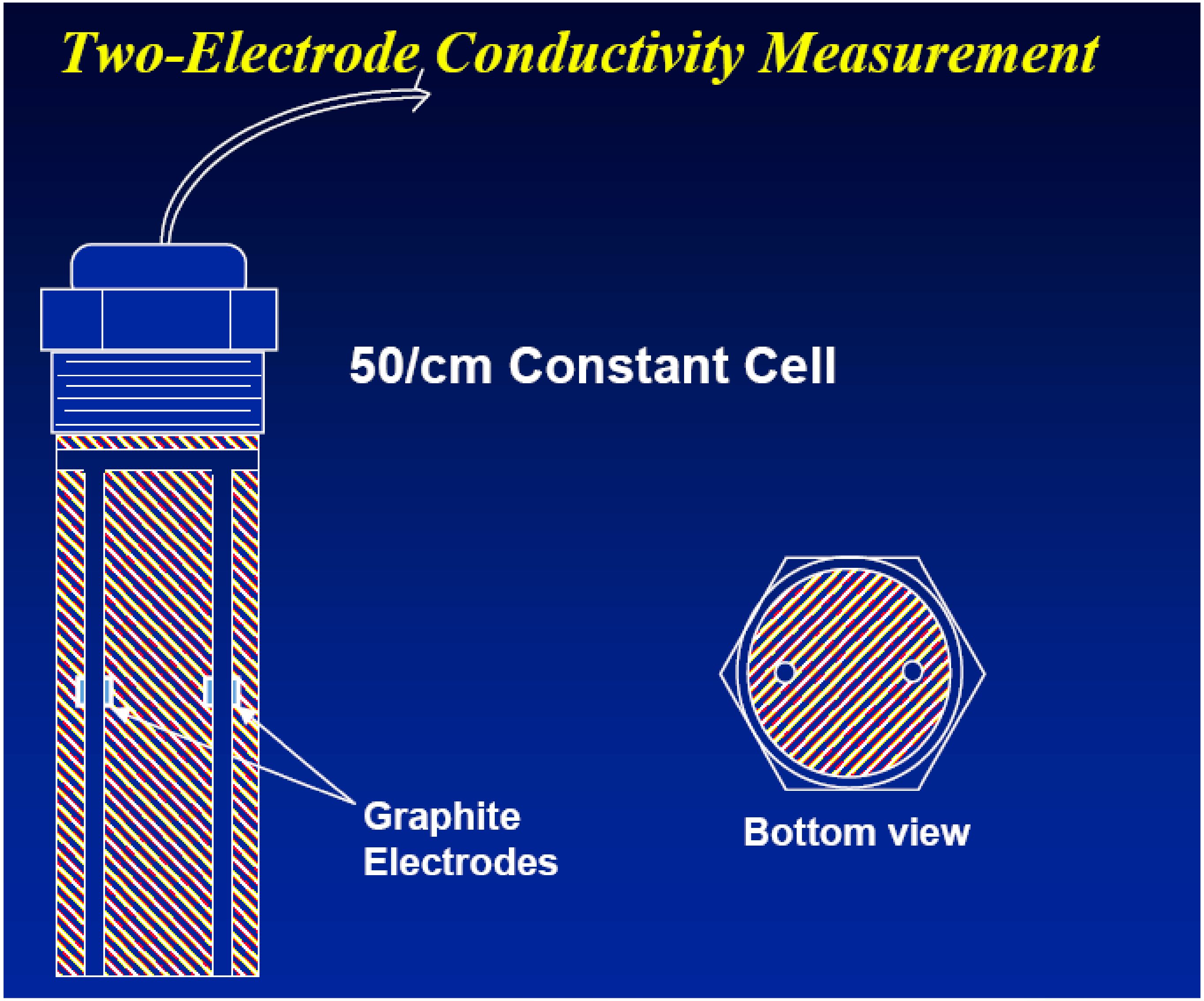


Specific conductivity (κ) = Measured conductivity (G) X electrode cell constant (L/A)

L: length of the column of liquid between the electrode
A: area of the electrodes

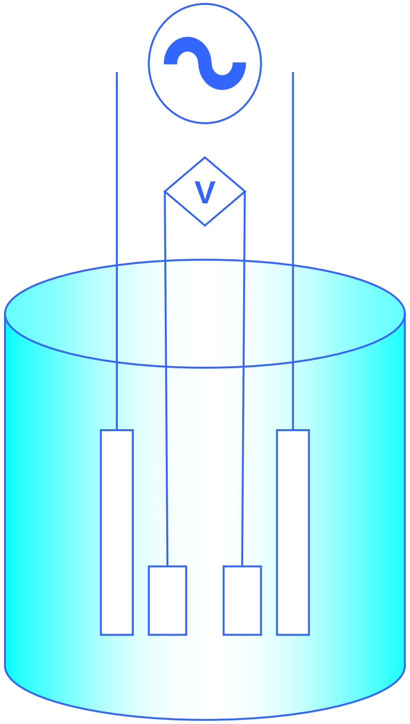
$$\kappa = G \times (L/A)$$

Conductivity



Conductivity

Four Electrode Conductivity Cells



- Measures Current and Voltage Drop
- Current Increases with an Increase in Voltage Drop Across Electrodes
- Compensates for Minor Coatings on Conductivity Electrodes
- Used for Higher Range Measurement

Conductivity

- Total dissolved solids (TDS):
  - Measure of total amount of all materials that are dissolved in water
  - These materials, both natural and made by humans
    - Inorganic solids, with a minor amount of organic material
  - Depending on the type of water, TDS can vary
  - Seawater contains 3.5% (35,000 mg/L) TDS
  - EPA Secondary Drinking Water Standards recommends that the TDS concentrations in drinking water not exceed 0.05% (500 mg/L), based on taste and aesthetics

Conductivity

Measuring TDS With Conductivity Method

- *TDS = 0.7 σ*
  - *σ = conductivity (μs/cm)*
- Electrical conductivity of water is directly related to the concentration of dissolved solids in the water
  - Ions from the dissolved solids in water influence the ability of that water to conduct an electrical current, which can be measured using a conductivity meter
  - When correlated with laboratory TDS measurements, electrical conductivity can provide an accurate estimate of the TDS concentration

Conductivity

Hardness

- Waters that contain a significant concentration of dissolved minerals like calcium, magnesium, strontium, iron, and manganese, are called "hard“
  - Because it takes a large amount of soap to produce a lather or foam with these waters.
- Total hardness is expressed as mg/L of calcium carbonate because calcium (Ca) and carbonate (CO_3) are dominant ions in most hard waters
- The following table gives concentration of $CaCO_3$ dissolved in water by its degree of hardness.

Degree of Hardness	**mg/L as $CaCO_3$**
Soft	0-60
Moderately Hard	60-120
Hard	120-180
Very Hard	Greater than 180

Conductivity

The conductivity and molar conductivity of a saturated aqueous solution of silver chloride are $3.41\times10^{-4}\,S\cdot m^{-1}$ and $138.26\times10^{-4}\,S\cdot m^{2}\cdot mol^{-1}$ respectively at 25°C. The conductivity of the water used to make the solution is $1.60\times10^{-4}\,S\cdot m^{-1}$ at the same temperature. Calculate the solubility of silver chloride in water at 25°C.

Conductivity

- **Solution** the conductivity of the silver chloride solution should be the sum of conductivities of silver chloride and water.

$$\begin{aligned}\kappa(\mathrm{AgCl}) &= \kappa(\mathrm{solution}) - \kappa(\mathrm{H_2O}) \\ &= (3.41\times10^{-4} - 1.60\times10^{-4})\mathrm{S\cdot m^{-1}} \\ &= 1.81\times10^{-4}\mathrm{S\cdot m^{-1}}\end{aligned}$$

- The solubility of silver chloride solution is then obtained

$$c = \frac{\kappa}{\Lambda_m} = \frac{1.81\times10^{-4}\mathrm{S\cdot m^{-1}}}{138.26\times10^{-4}\mathrm{S\cdot m^2\cdot mol^{-1}}} = 0.01309\mathrm{mol\cdot m^{-3}}$$